GLOBAL R&D

TUESDAY, JANUARY 17, 2017

FAT CRYSTALLITE THICKNESS DISTRIBUTIONS

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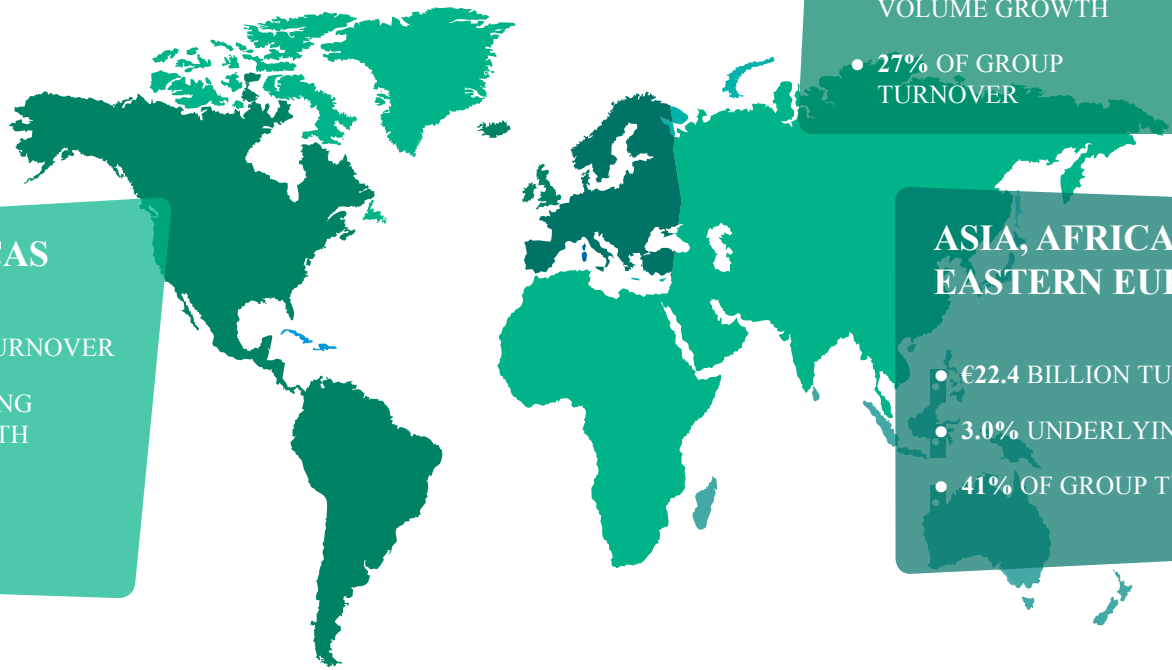
UNILEVER IS A GLOBAL COMPANY

EUROPE

- **€13.6** BILLION TURNOVER
- **2.6%** UNDERLYING VOLUME GROWTH
- **27%** OF GROUP TURNOVER

THE AMERICAS

- **€17.3** BILLION TURNOVER
- **0.4%** UNDERLYING VOLUME GROWTH
- **32%** OF GROUP TURNOVER



ASIA, AFRICA, CENTRAL & EASTERN EUROPE

- **€22.4** BILLION TURNOVER
- **3.0%** UNDERLYING VOLUME GROWTH
- **41%** OF GROUP TURNOVER

2015 TURNOVER = €53.3 BN

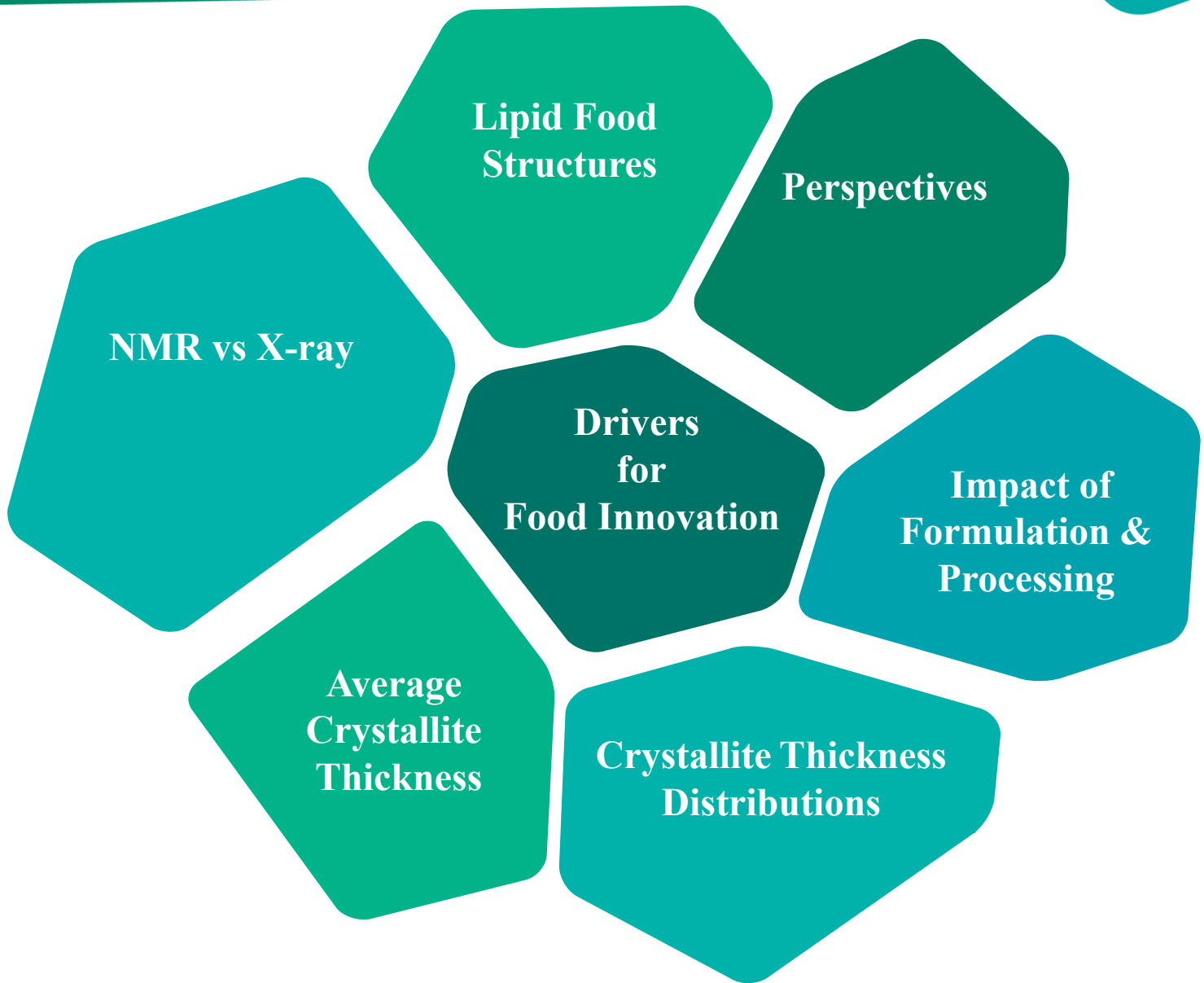
R&D FACTS & FIGURES

- **€1 billion** annual investment
- **>6,000** R&D professionals
- **6** key R&D sites; **92** locations around the globe
- Portfolio of **>20,000** patents and patent applications
  >300 new patent applications filed each year;
  Most active patent applicant in UK in 2013
- **64** research publications in 2015

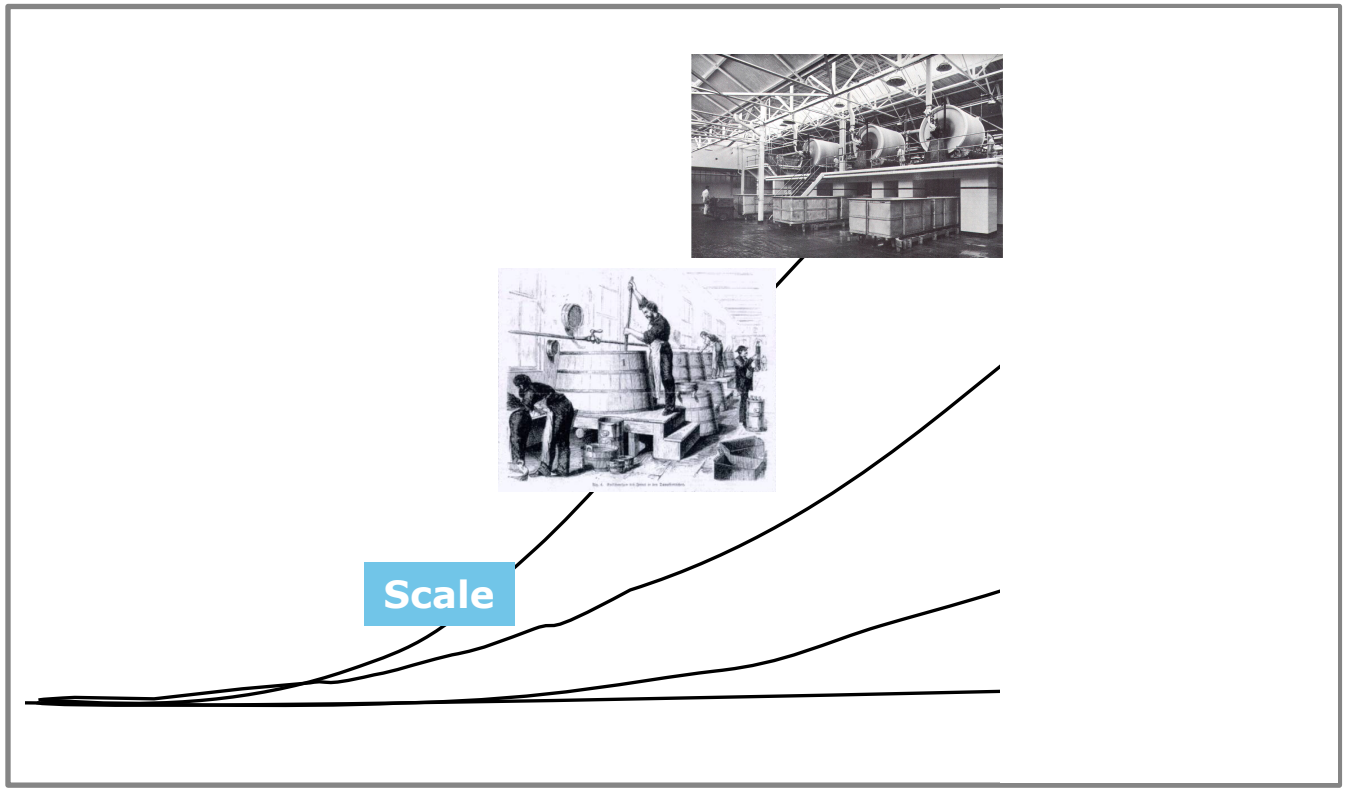
WORKING WITH OTHERS

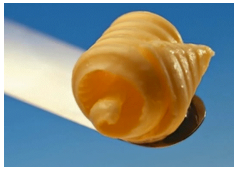
- 14 Top Universities
- 18 Global Partners

OUTLINE


Lipid Food Structures
Perspectives
NMR vs X-ray
Drivers for Food Innovation
Impact of Formulation & Processing
Average Crystallite Thickness
Crystallite Thickness Distributions

FOOD INNOVATION: AN OLD TRADE

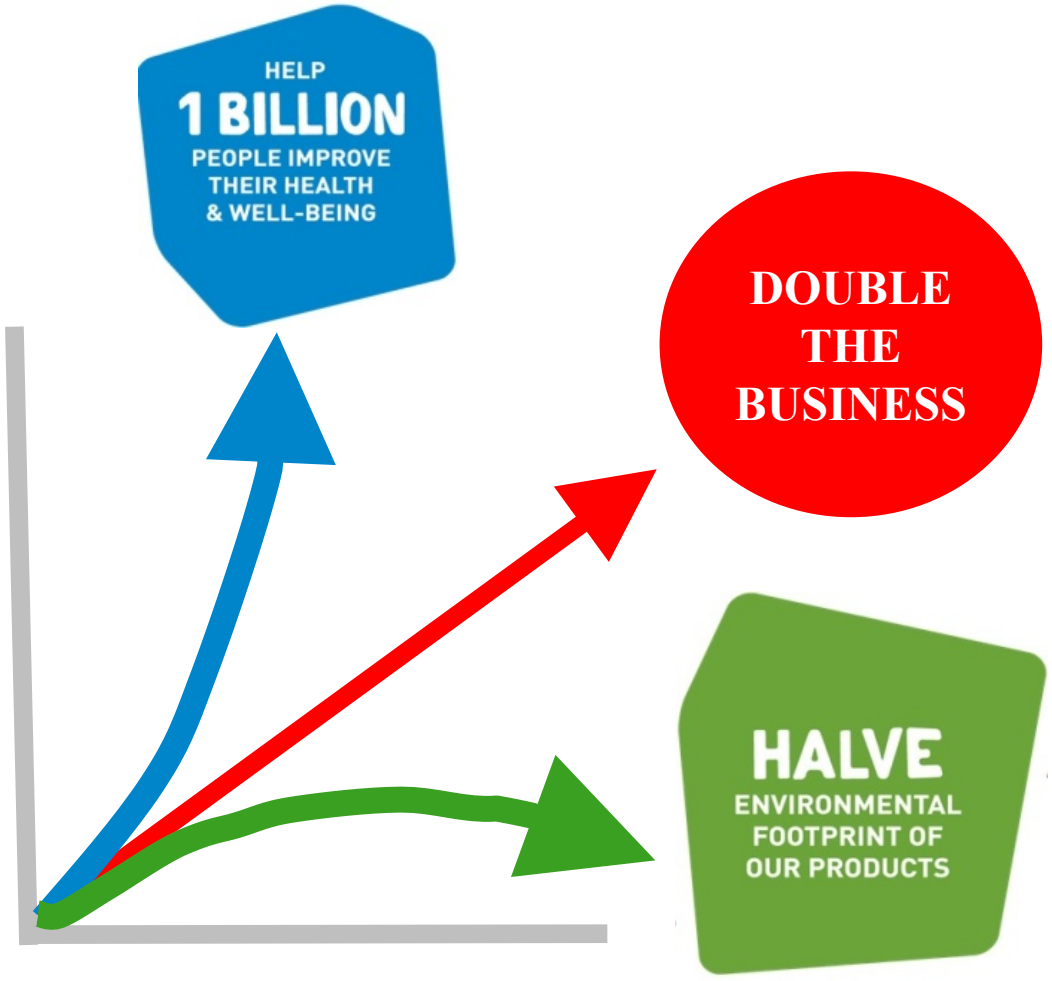




POSITIVE SOCIAL IMPACT

REDUCE ENVIRONMETNAL FOOTPRINT

OUR MOTIVATION



QUITE SOME DEMANDS

Affordable
Safe

HELP
1 BILLION
PEOPLE IMPROVE
THEIR HEALTH
& WELL-BEING

HALVE
ENVIRONMENTAL
FOOTPRINT OF
OUR PRODUCTS

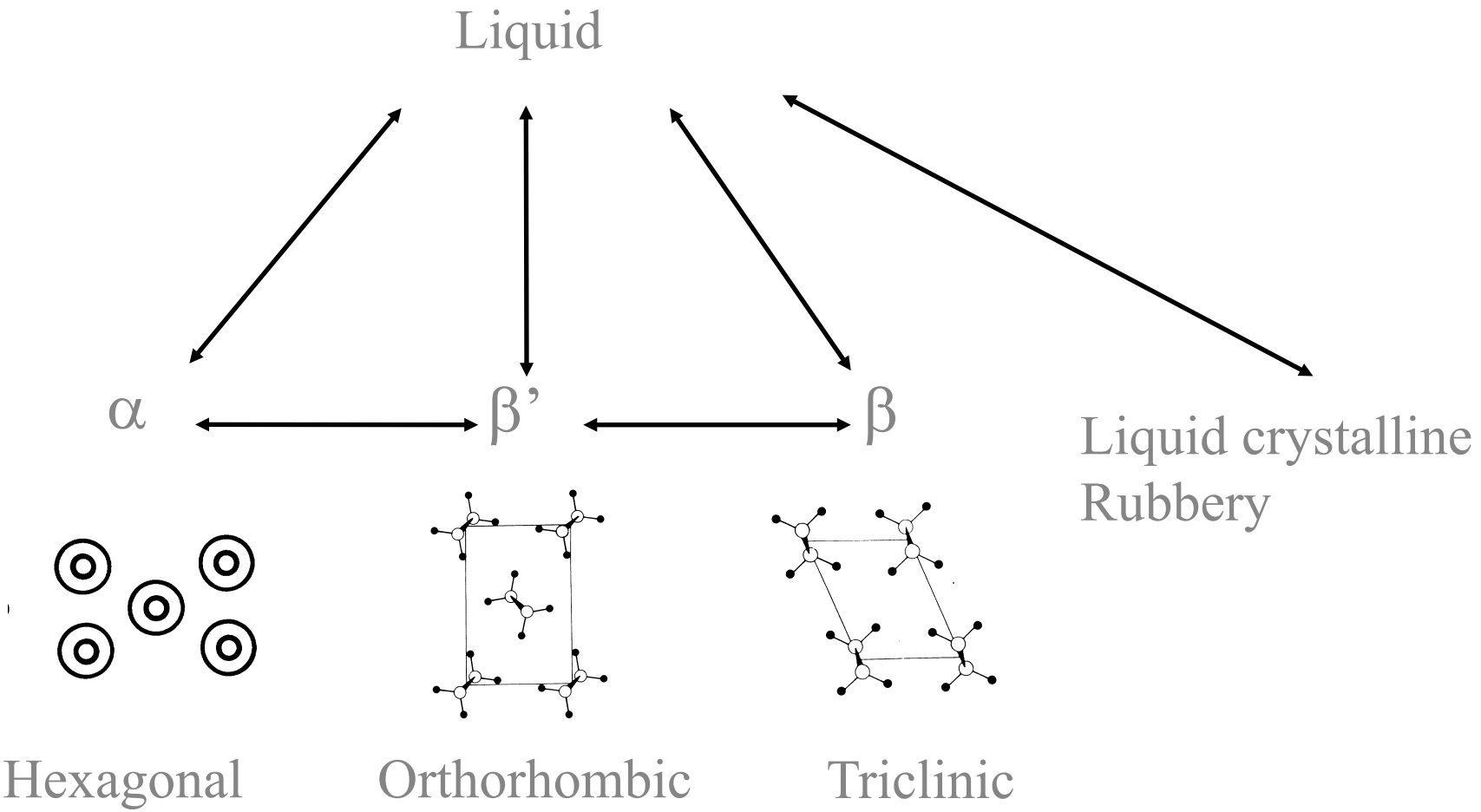
Convenience

FOOD LIPID STRUCTURES

MULTISCALE FOOD LIPID STRUCTURES

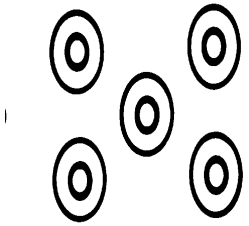
NMR VS X-RAY CRYSTALLOGRAPHY

FAT CRYSTAL POLYMORPHISM

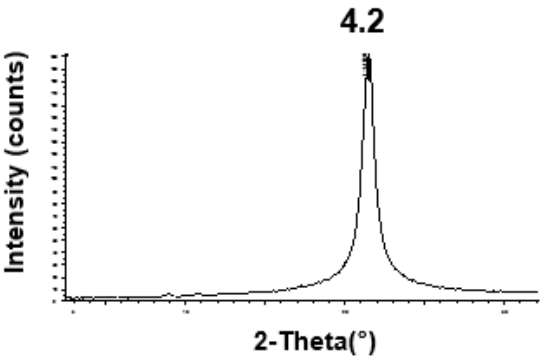


LIPID POLYMORPHISM: THE X-RAY VIEW

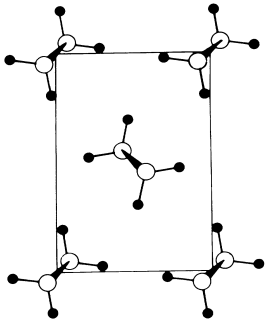
α



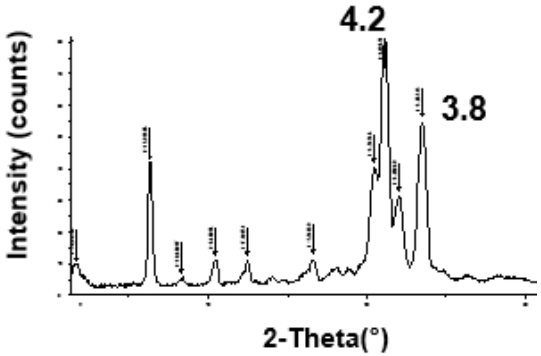
Hexagonal



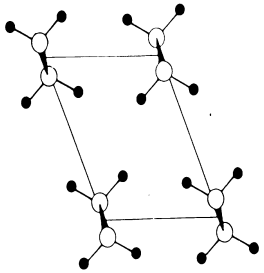
β'



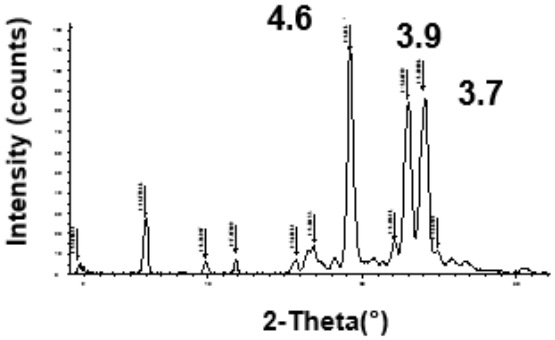
Orthorhombic



β



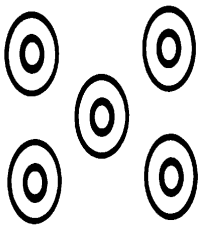
Triclinic



d-values in Ångström

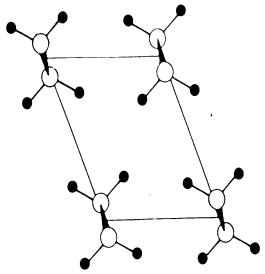
LIPID POLYMORPHISM: THE NMR VIEW

α



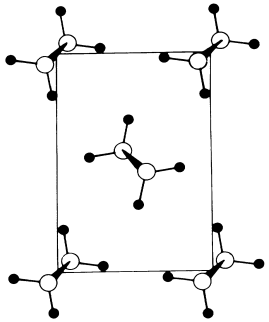
Hexagonal

β

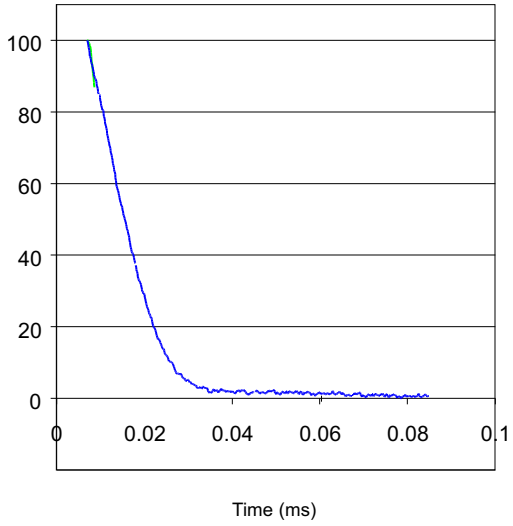


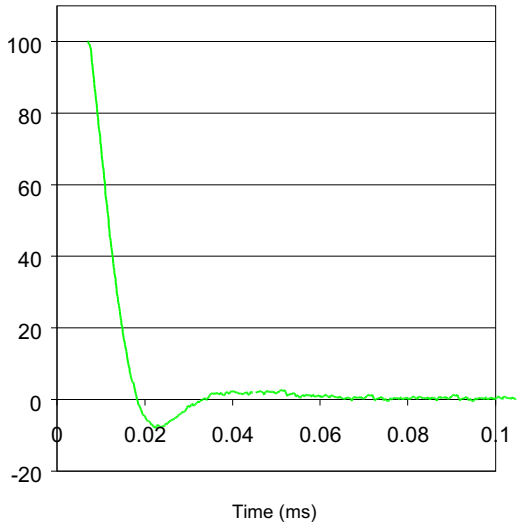
Triclinic

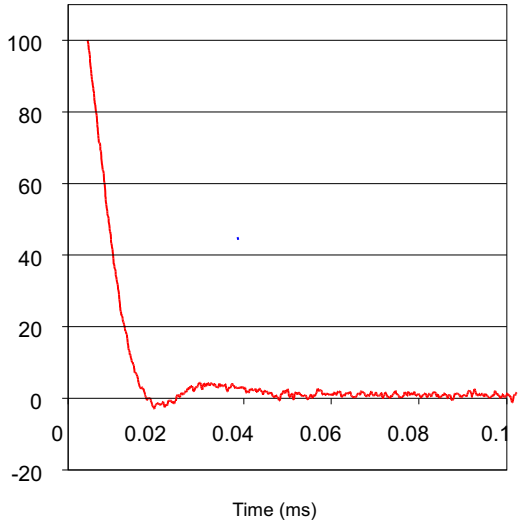
β’



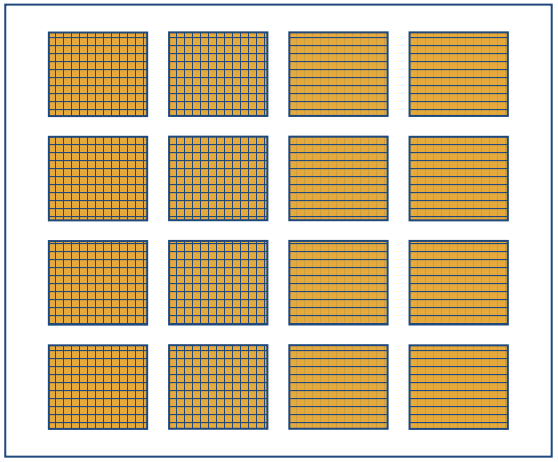
Orthorhombic

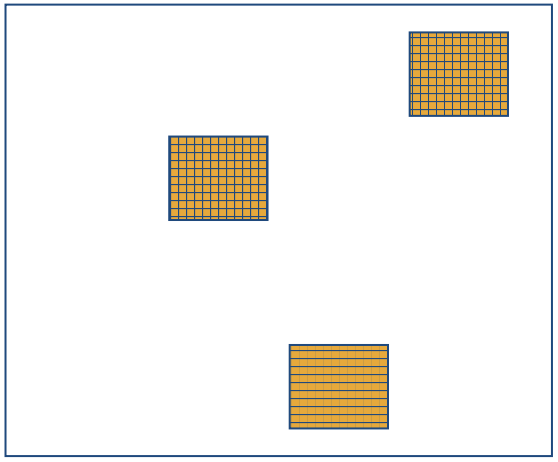






X-RAY VS NMR



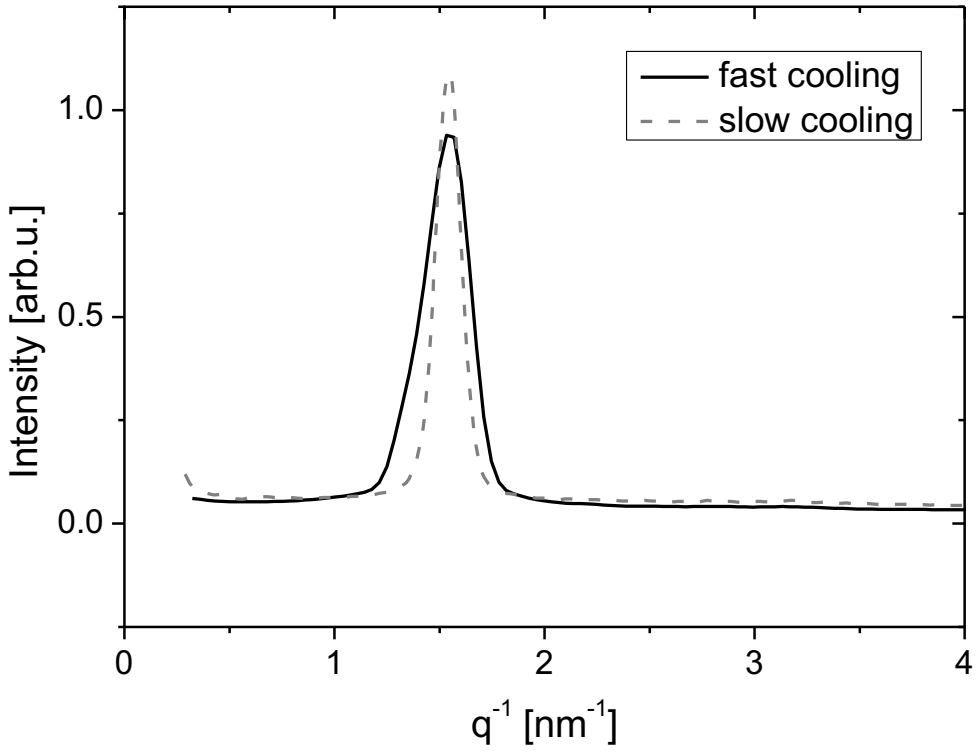


X-ray
Periodicity needed

NMR
Local order & dynamics
No long-range order needed

AVERAGE CRYSTALLITE THICKENESS

THE X-RAY VIEW: DIFFRACTION PEAK WIDTH



THE (simple) X-RAY VIEW
1. The Scherrer equation

- Peak broadening due to
  - crystallite size
  - instrument
  - microstrains

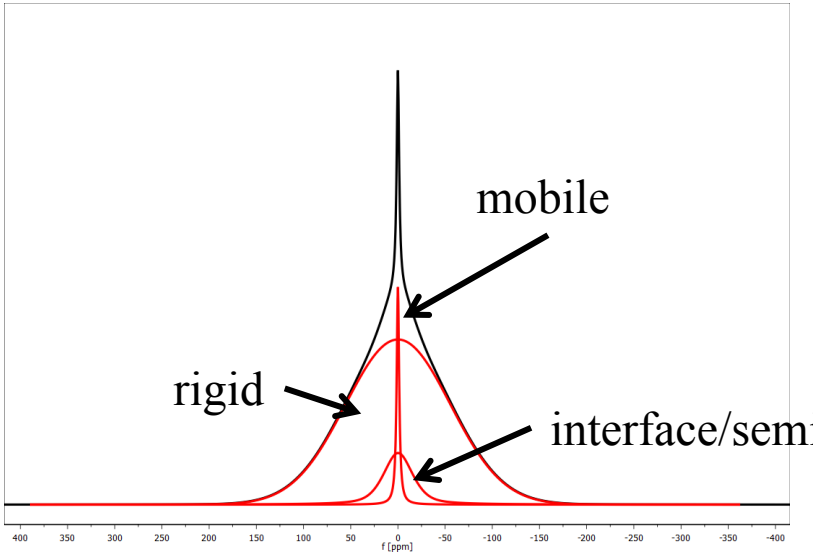
Scherrer equation for average crystallite thickness (ACT)

$$\Delta(2\theta) = \frac{K\lambda}{ACT\cos\theta}$$

K depends on

- how the peak width is defined
- the shape of the crystal/crystallite
- the size distribution

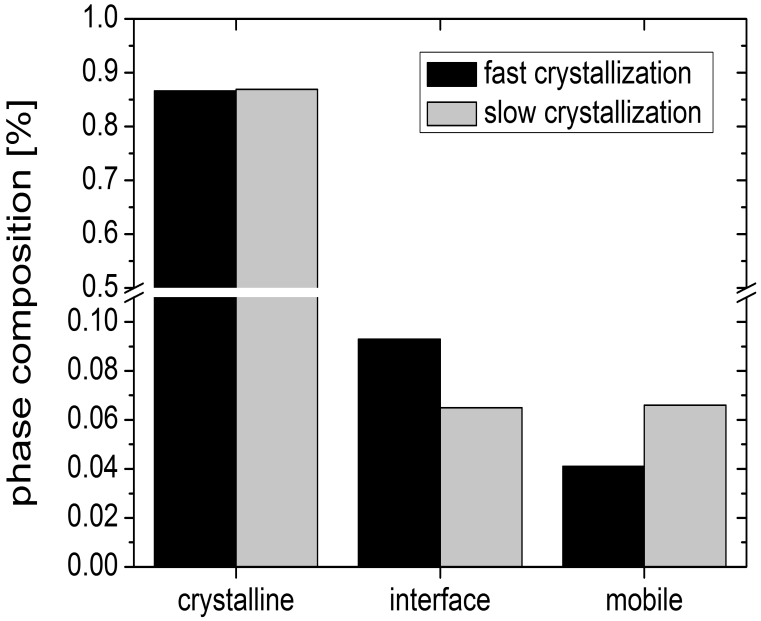
THE NMR VIEW: LOCAL DIFFERENCES IN MOBILITY



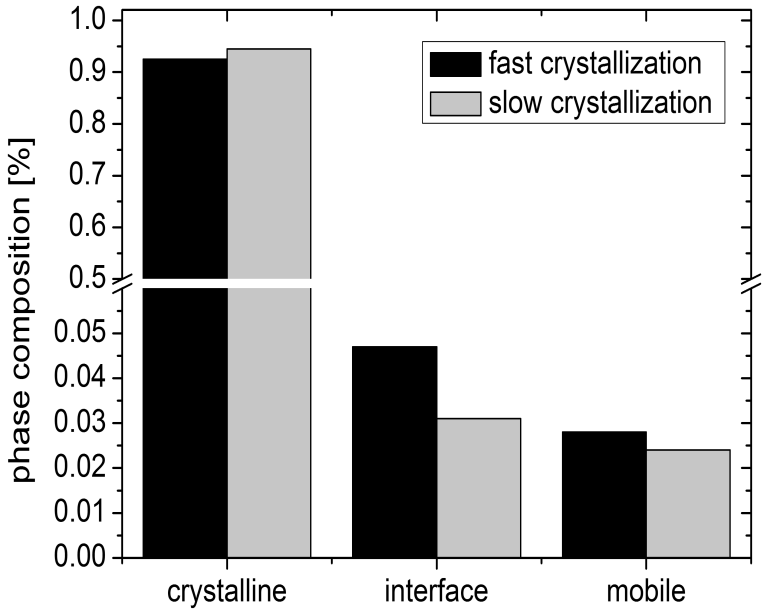
^{1}H spectrum of a fat blend.

THE NMR VIEW: LOCAL DIFFERENCES IN MOBILITY

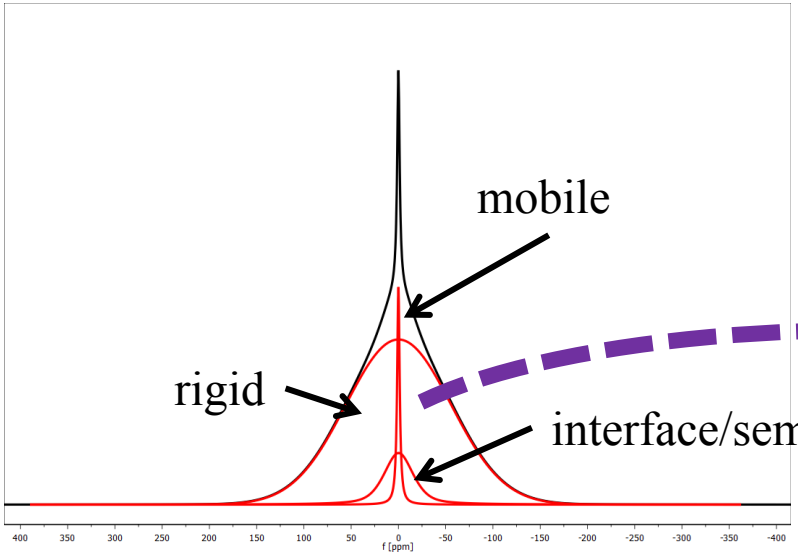
Blend A



Blend B

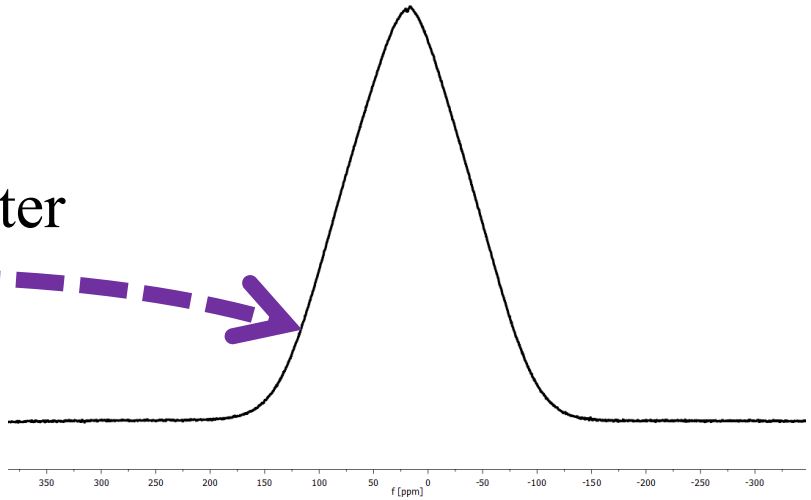


NMR SELECTION OF RIGID DOMAINS



1H spectrum of a fat blend

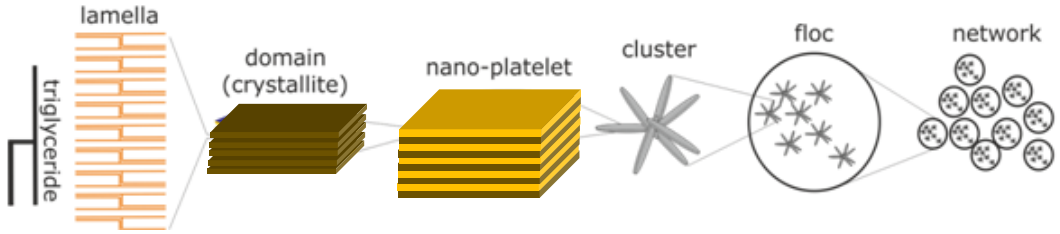
DQ filter



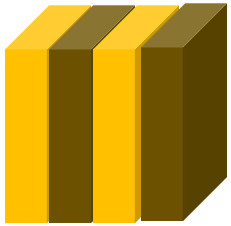
DQ edited spectrum, rigid phase selected.

THE NMR VIEW ON THICKNESS: SPIN-DIFFUSION

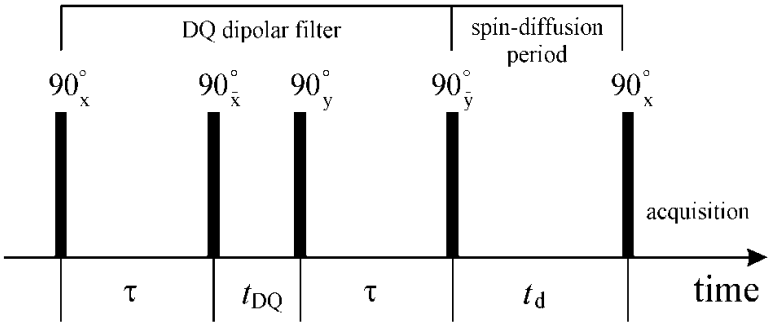
Multi-scale structures



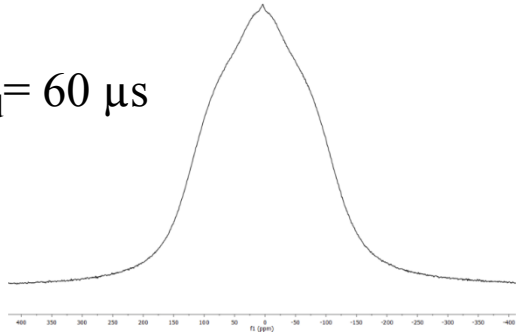
Å nm µm mm



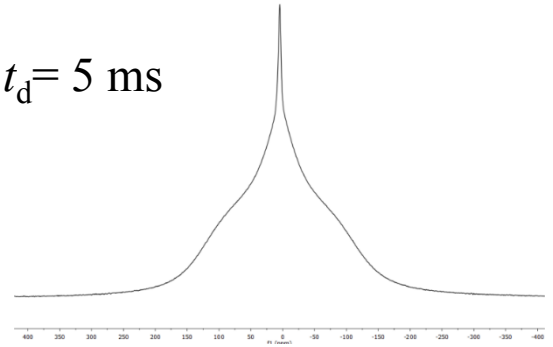
THE NMR VIEW ON THICKNESS: SPIN-DIFFUSION



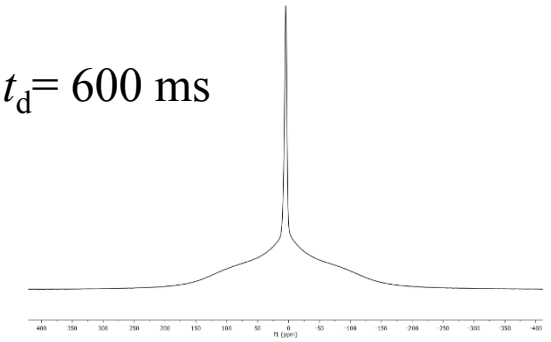
t_d= 60 µs



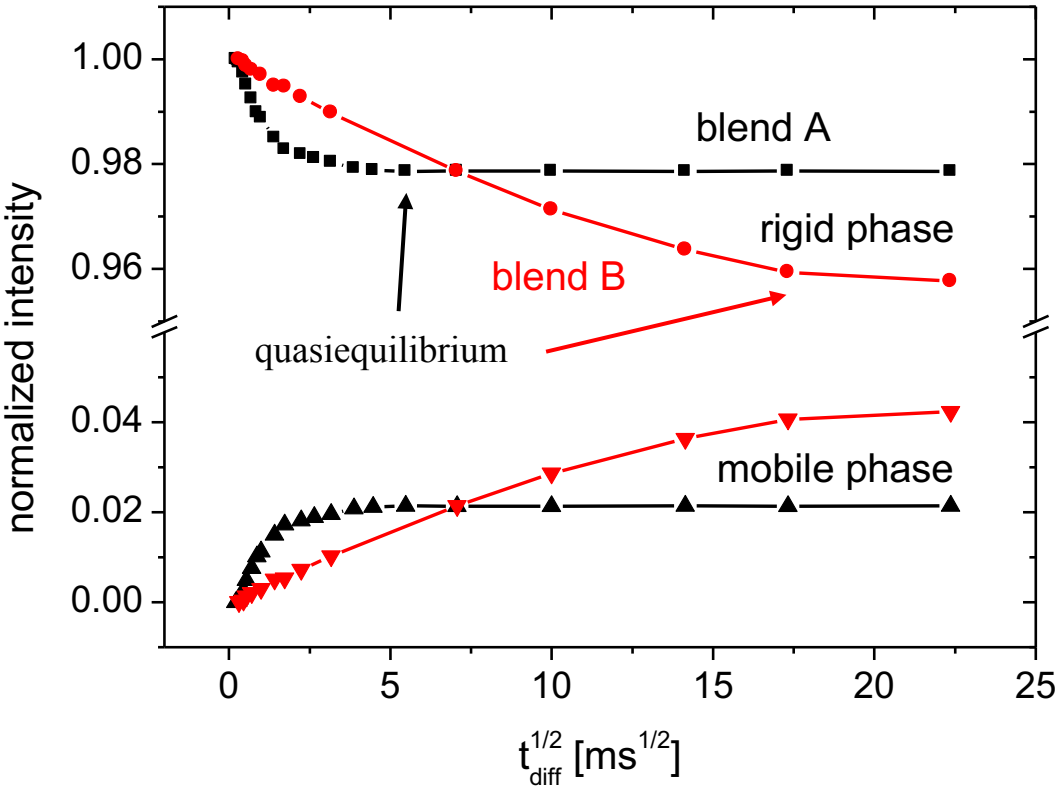
t_d= 5 ms



t_d= 600 ms



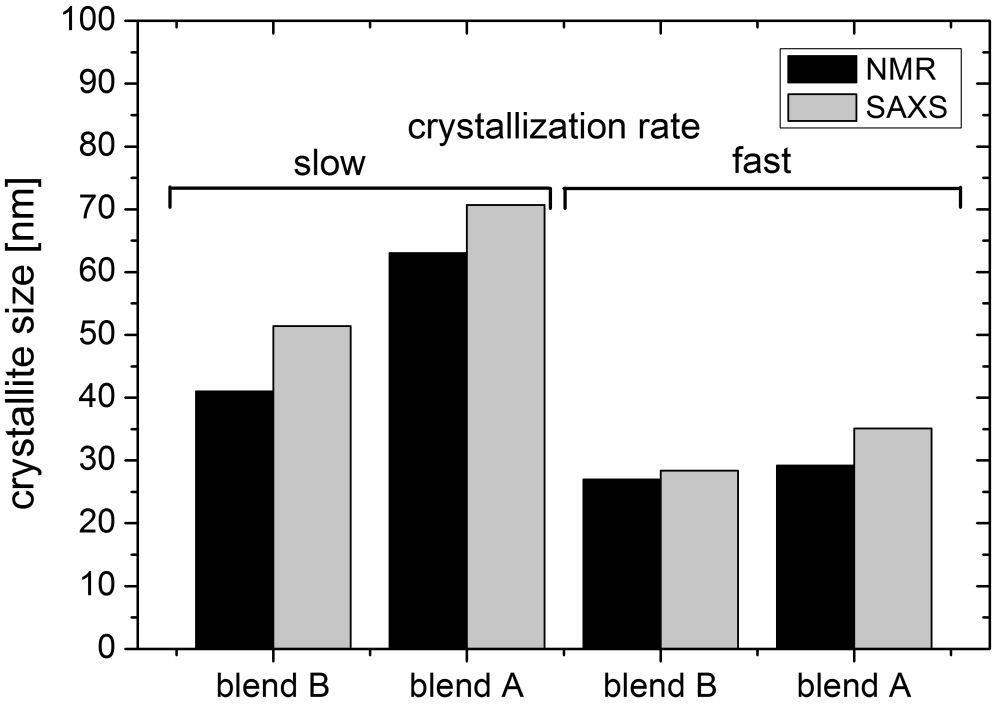
THE NMR VIEW ON THICKNESS: SPIN-DIFFUSION



Fatty acid	Blend A	Blend B
C18:0	5%	13%
C16:0	50%	8%
C14:0	7%	14%
C12:0	20%	50%
C18:x	12%	6%
Others	6%	9%

AVERAGE CRYSTALLITE THICKNESS by NMR and SAXS

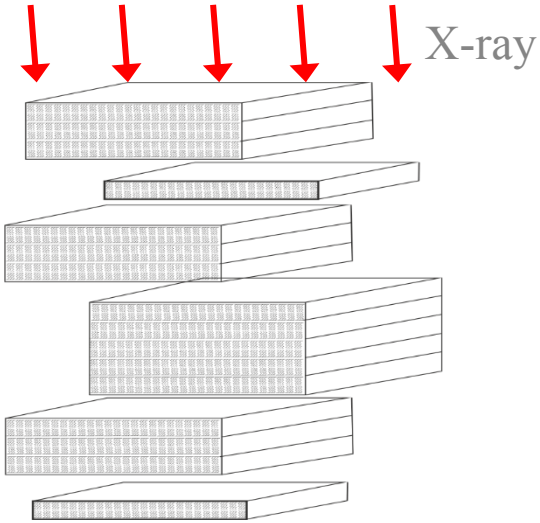
Operational range



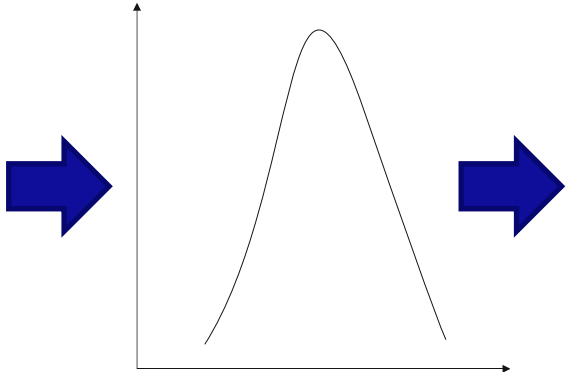
- **Operational range: <100 nm**
- **Assumption: unimodal distribution**
- **NMR biased to smaller thicknesses: heterogeneity?**

CRYSTALLITE THICKNESS DISTRIBUTIONS

FROM AVERAGE TO THICKNESS DISTRIBUTION



Diffraction line from all crystals



Fourier series

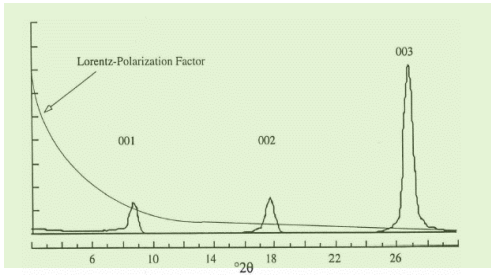
$$S = \sum_{n(all\ crystals)} A\,(n) * \cos 2\pi ns$$

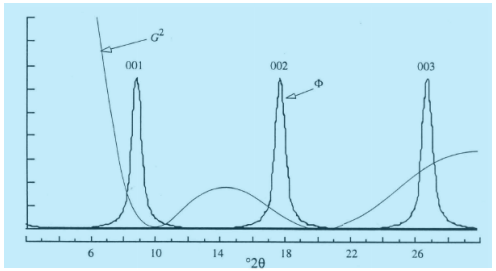
- The diffraction function can be expressed as a Fourier series dependent on all thicknesses (Bertaut-Warren-Averbach method, BWA).
- .Implemented in MUDMASTER programme

Bertaut-Warren-Averbach (BWA)

$$I(2\theta) = L_p(2\theta)\,G^2(2\theta)\,\Phi(2\theta)$$

Lorentz factor — structure factor — interference function





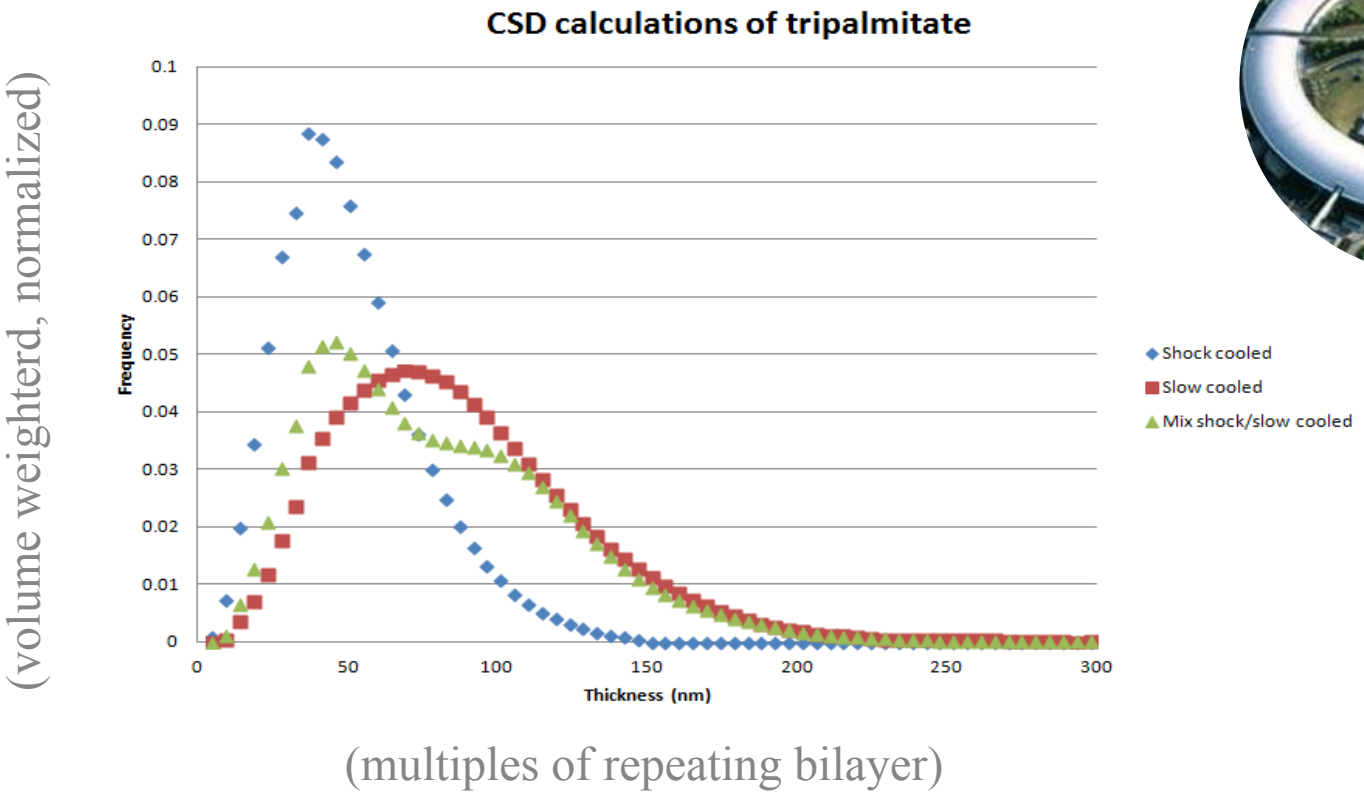
$$\sum H(n)\cos 2\pi n s^*$$

Thickness distribution M: $\mathbf{H(n) = \frac{1}{M}\sum(M - n)f(M)}$

THE MUDMASTER COOKBOOK FOR RETRIEVING CTD

- Read the XRD peak $I(\theta)$
- (Correct for Lp G^2)
- Remove background
- Correct for instrumental broadening
- Decompose ϕ into Fourier series H
- Determine thickness distribution M

VALIDATION



(volume weighterd, normalized)

(multiples of repeating bilayer)

IMPACT OF PROCESSING

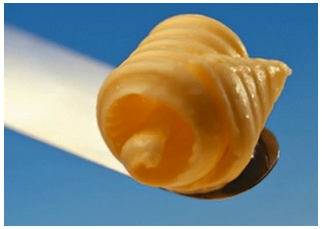
SPREADS MANUFACTURING

Conventional Formulation

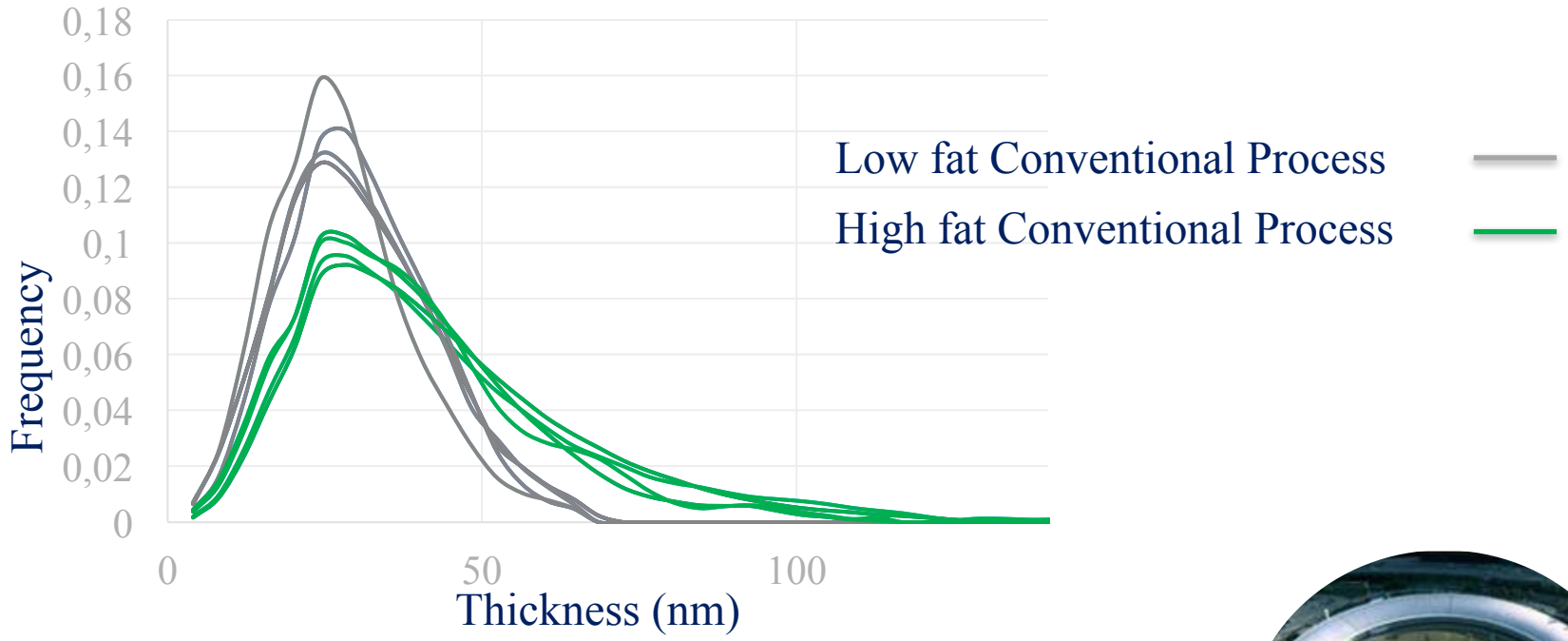
oil/fat blend
Water

Conventional Process

Melt/cool: fat crystallization
X
Mix: emulsification



CONVENTIONAL PROCESSING
Impact of formulation



SPREADS MANUFACTURING

Conventional Formulation

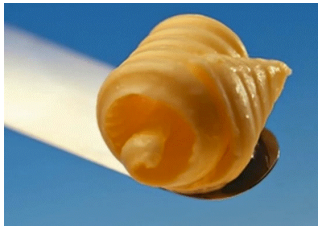
oil/fat blend
Water

Novel formulation

oil
solid fat powder
water

Conventional Process

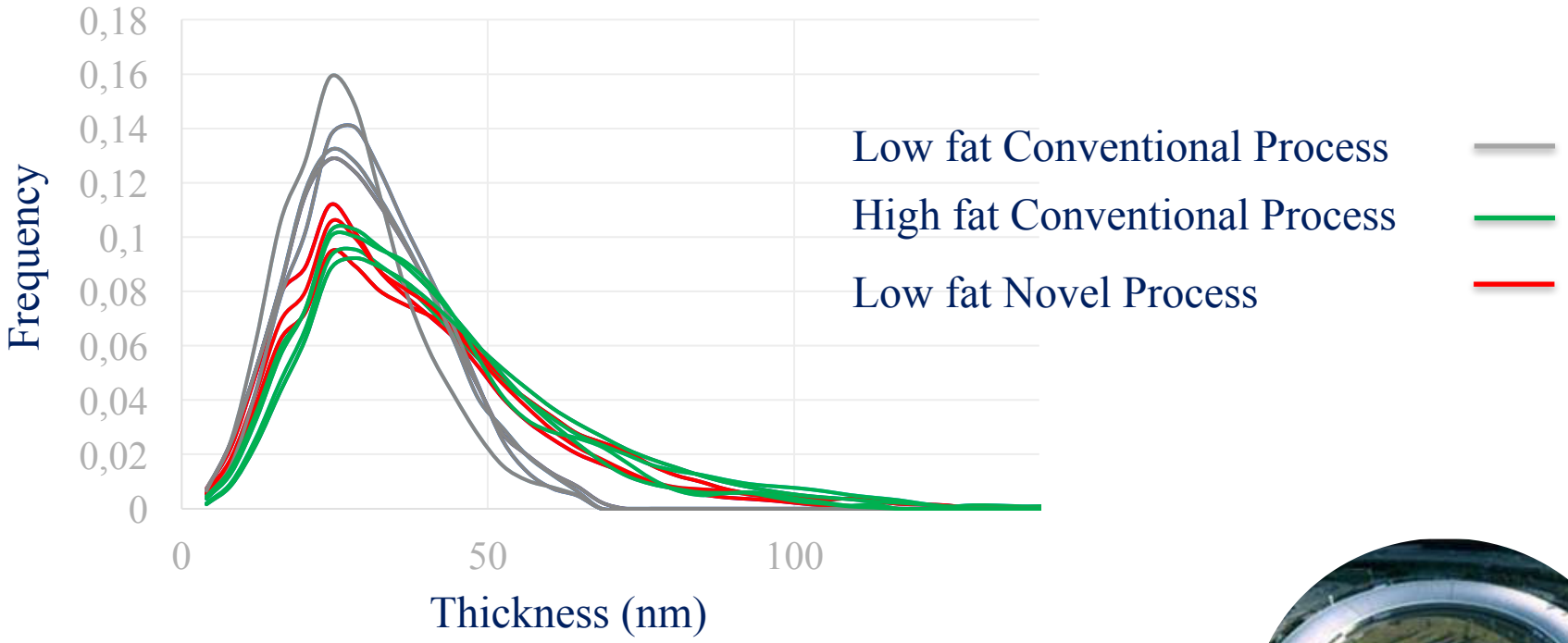
Melt/cool: fat crystallization
X
Mix: emulsification



Novel process

Mix: emulsification

NOVEL PROCESSING
Impact of processing



CONCLUSIONS

NMR and SAXS quantitatively assess average crystallite thickness

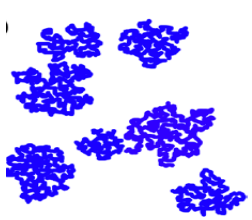
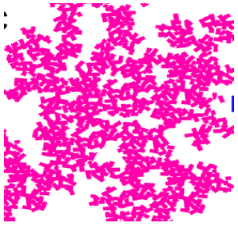
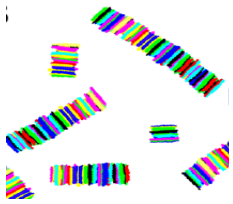
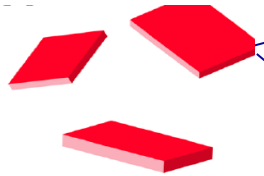
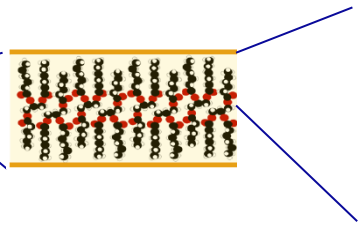
WBA method accurately determines thickness distribution

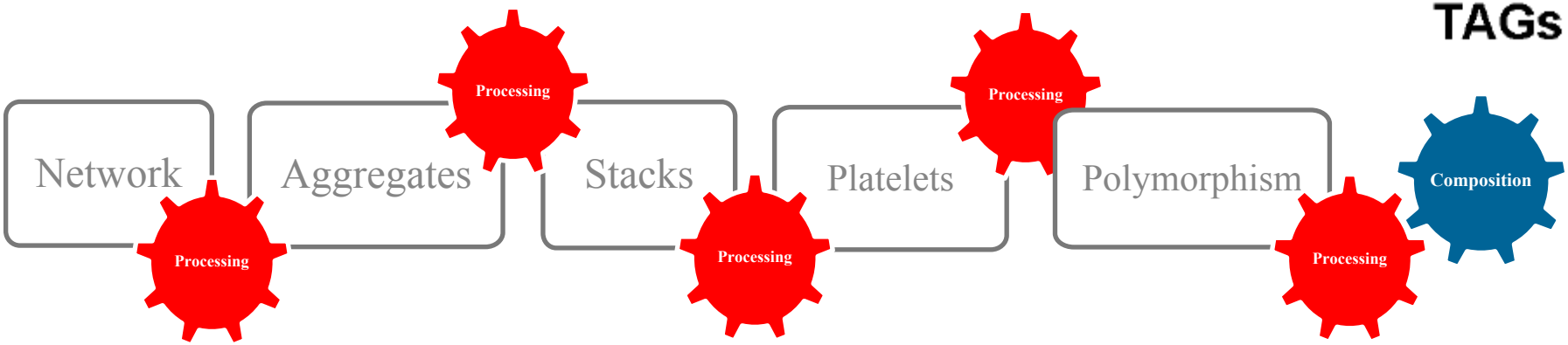
Processing conditions leave a fingerprint in crystallite thickness distributions

Methodology for benchmarking food formulation &processing

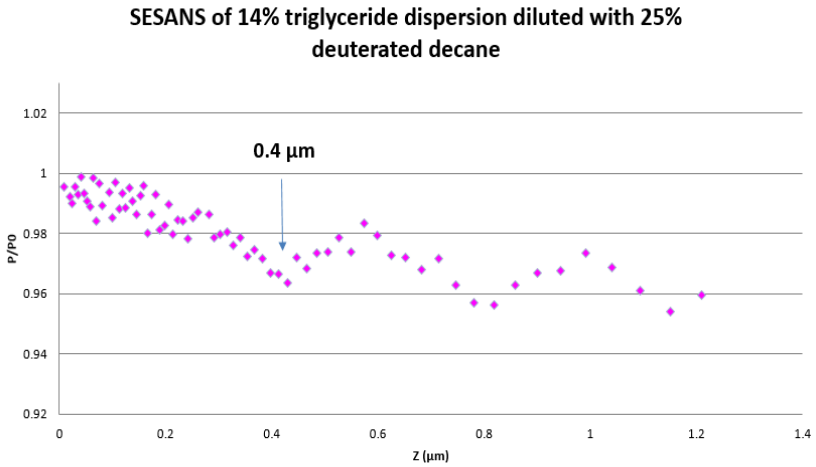
Definition and protection of IP on novel processing routes

MULTISCALE FOOD LIPID STRUCTURES

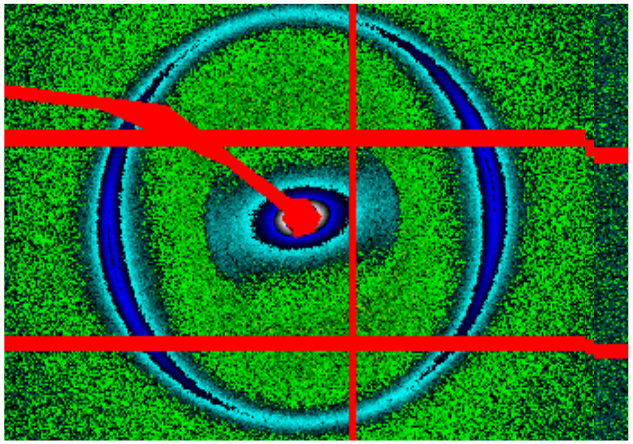






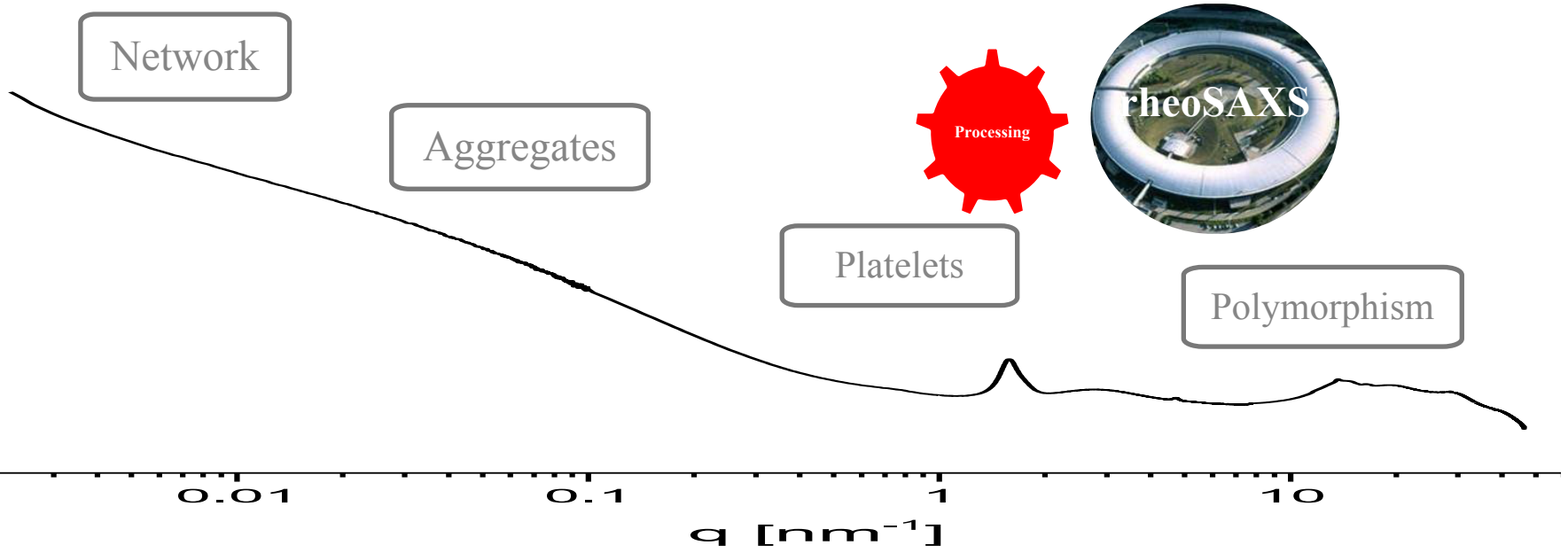


PERSPECTIVES: SESANS



PERSPECTIVES: SAXS UNDER SHEAR





ACKNOWLEDGEMENTS

Ruud den Adel

Kees van Malssen

Michiel Meeuse

Adrian Voda

Oleksandr Mykjaylyk

Tatiana Nikolaeva

Henk Van As

Wim Bouwman

Evgenii Velichko

Physical meaning of the interference function

- The interference function represents effects of the phase differences that appear during wave scattering by all the n^{th} nearest layer pairs that exist in the stacks.

- *m, m'* are 2 layers separated by $n = m'-m$ interlayer spacings $d(001)$ Distance between *m* and *m'* is $Z_n = nd(001)$.

- The contribution to diffraction due to the phase differences between the 2 waves is expressed by the term
  - $\cos(2\pi Z_n Z^*)$

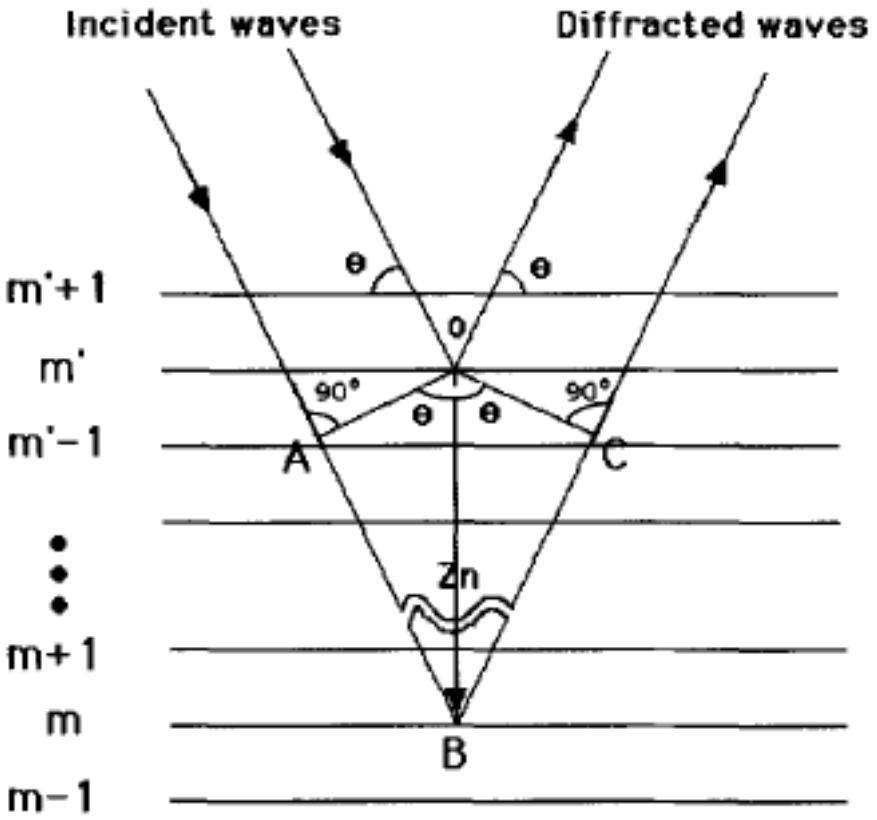


Figure 1. A schematic illustrating the difference in paths traveled by diffracted waves scattered by m' and m layers separated by *n* interlayer spacings ($n = m' - m$), so that the distance between the layers $Z_n = m'd(001) - md(001) = nd(001)$.

$$Z^* = 2 \sin \theta/\lambda$$

Physical meaning of the interference function

- The summation of these cos(…) products for all $n = m' - m$ normalized for the unit cell (divided by total number of layers, M), gives the interference function, $\phi(Z^*)$.
- $\phi(Z^*)$ describes the total effect of the phase difference on the intensity distribution along the Z^* axis:

$$\phi(Z^*) = \sum_{n=-M}^{M} \frac{(M - |n|)}{M} \cos 2\pi Z_n Z^*$$

- It is physically unrealistic to assume that samples consist of stacks having the same number of layers.

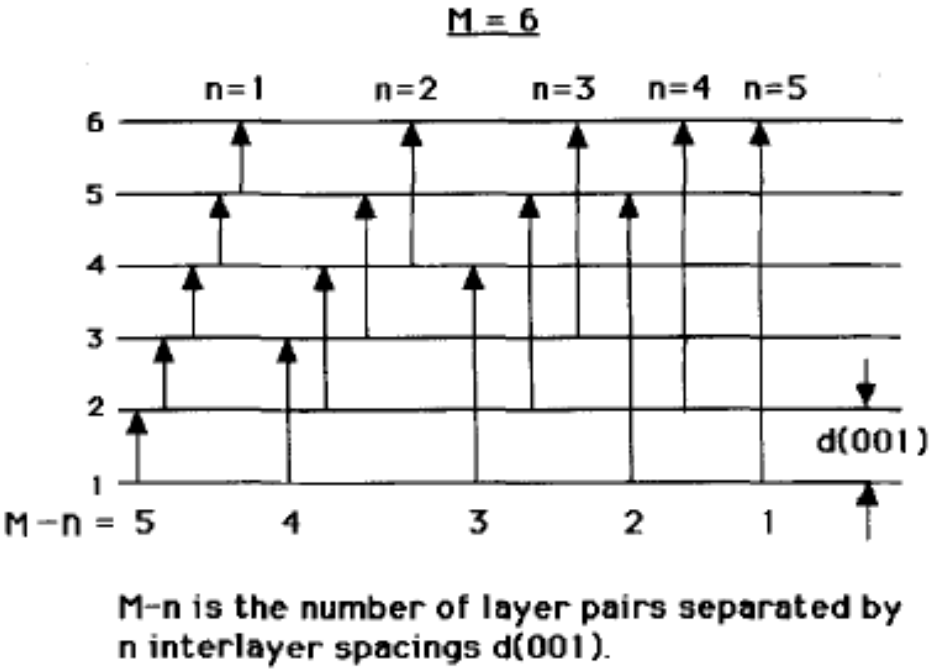


Figure 2. Relation between total number of layers in a crystal (M) and amount of pairs of layers ($M - n$) separated by n spacings of $d(001)$. An increase in n from 1 to 5 decreases the number of nth neighbors from 5 to 1.

Physical meaning of the interference function

- Realistic situation: the sample consists of a stack with a distribution of layer thickness $f(M)$

$$\sum_{M_1}^{M_2} f(M) = 1 \quad \text{and} \quad \sum_{M_1}^{M_2} Mf(M) = \overline{M}$$

- M_1 and M_2 correspond to stacks having the smallest and the largest number of layers respectively.
- $\bar{M}$ is the mean number of layers per stack.

- The interference function for a sample having of a CTD:

$$\phi(Z^*) = \sum_{n=-M_2}^{M_2} \frac{N(n)}{\overline{M}} \cos 2\pi Z_n Z^* = \sum_{n=-M_2}^{M_2} H(n) \cos 2\pi Z_n Z^*$$

$$H(n) = \frac{1}{\overline{M}} \sum_{M_1}^{M_2} (M - n) f(M)$$

The interference function as a Fourier series

- After some math cosmetics on the equation of $\phi(Z^*)$…

$$\phi(Z^*) = \phi(s^*) = \sum_{n=-M_2}^{M_2} H(n)\cos 2\pi n s^*$$

- Because n is integer $\phi(s^*)$ represents a Fourier series.

- The Fourier coefficients $$H(n) = \frac{1}{M}\sum_{M_1}^{M_2}(M - n)f(M)$$

Determination of $f(M)$ and $\bar{M}$

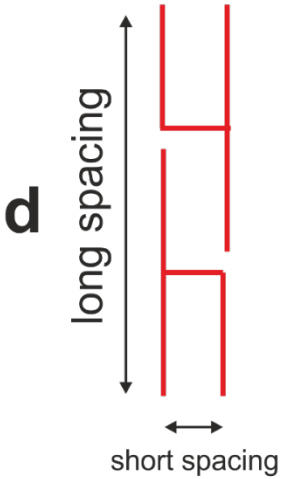
- $H(n)$ is a function dependent on the mean thickness and on the thickness distribution.

$$H(n) = \frac{1}{\bar{M}} \sum_{M_1}^{M_2} (M - n) f(M)$$

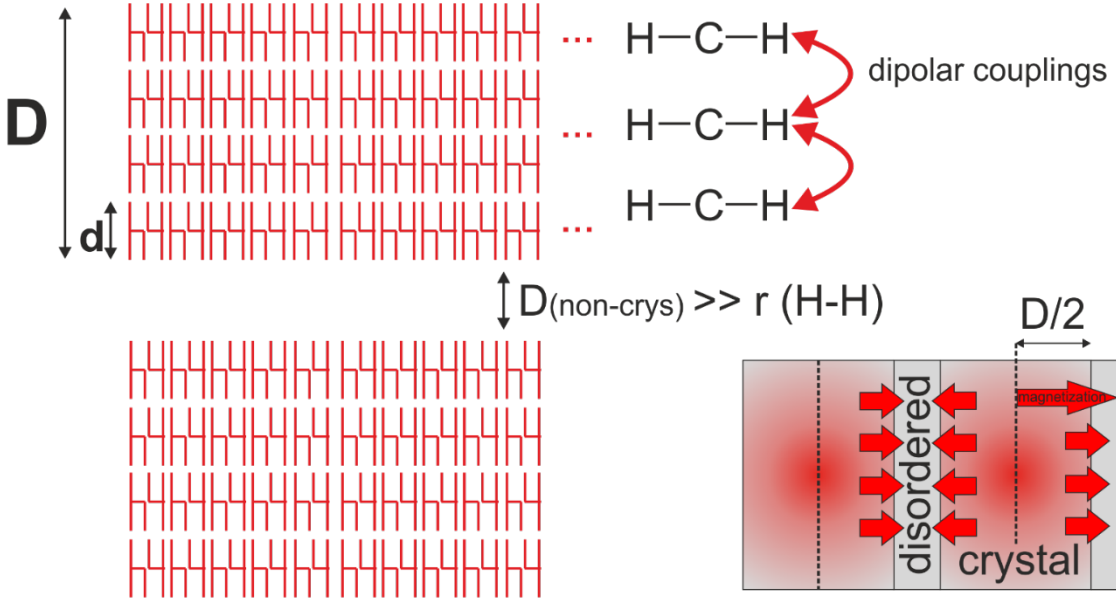
$$\left.\frac{\partial H(n)}{\partial n}\right|_{n \to 0} = \frac{1}{\bar{M}}, \quad \text{and} \quad \left.\frac{\partial^2 H(n)}{\partial n^2}\right|_{n \to 0} = \frac{f(M)}{\bar{M}}$$

Stack thickness (crystallite): $T = M \cdot d(001)$

MODELLING SPIN DIFFUSION



XRD

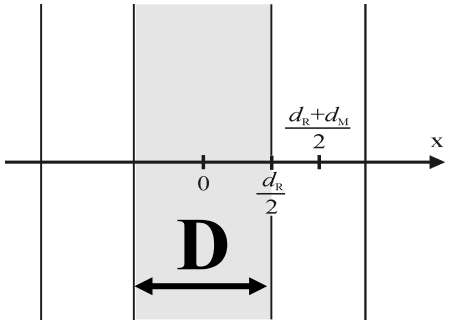


NMR spin-diffusion from fat crystallite to disordered phase via proton dipolar couplings.

NMR model

One approach solution:

$$D \cong \frac{4}{\sqrt{\pi}} \frac{\rho_M \sqrt{D_R D_M}}{\rho_R \sqrt{D_R} + \rho_M \sqrt{D_M}} \sqrt{t_0}$$



Fluctuations in the layer position/thickness

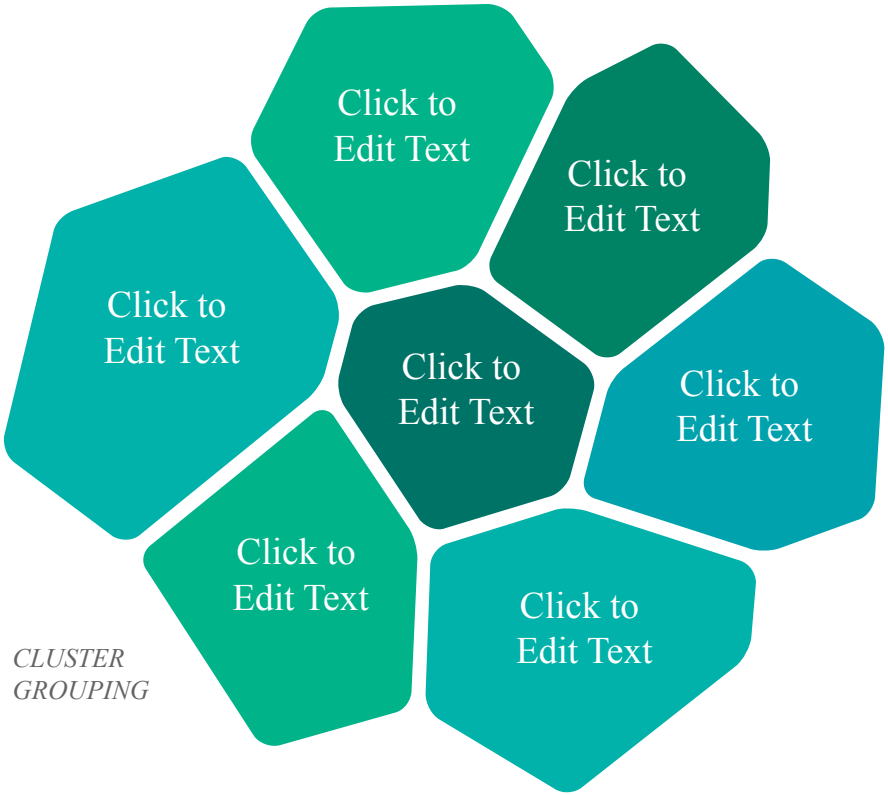
- This is about statistical variations of $d(001) \pm \varepsilon$.

- Implication to $\phi(Z^*)$ is that the cos() terms need averaging.

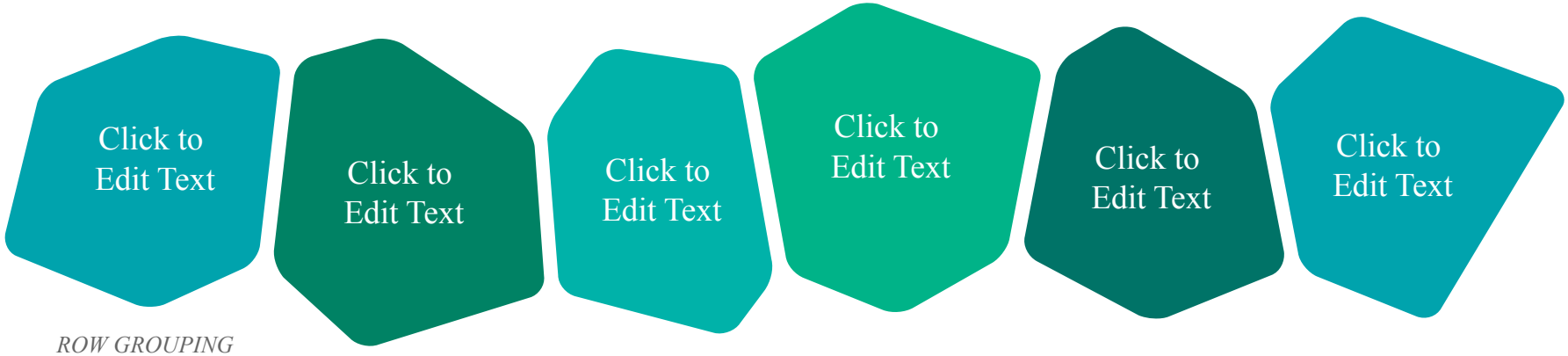
USING SEGMENTS

Use these shapes with text for optional placement in your layout. You can scale them, crop them off a page, and change their colour (within the chosen teal palette). You can use the segment shapes on their own, or in the groupings as shown.

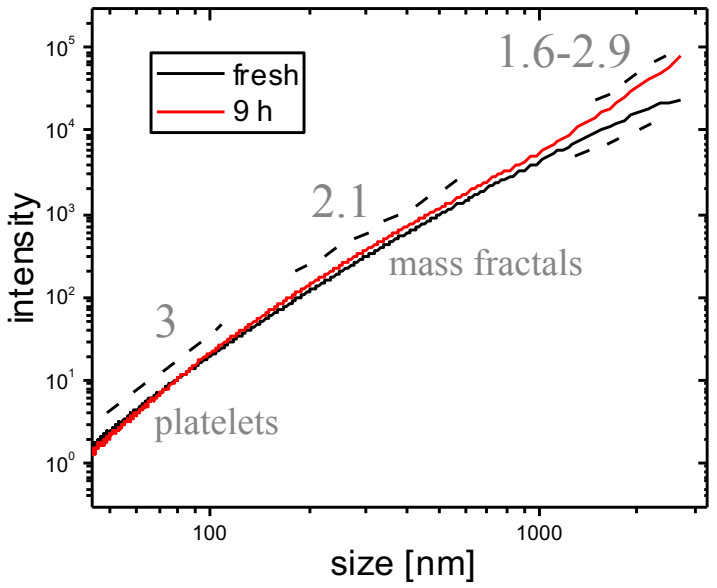
*Refer to the **Visual Identity Standards Guide** on the Brand Centre for more details on proper use.*



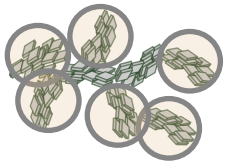
CLUSTER GROUPING



ROW GROUPING



Larger aggregates
-fresh slurry: DLCA aggregates (fractal d=1.6)
-aged 9h: fractal dimension increases with ageing (2.9)
-age dependent



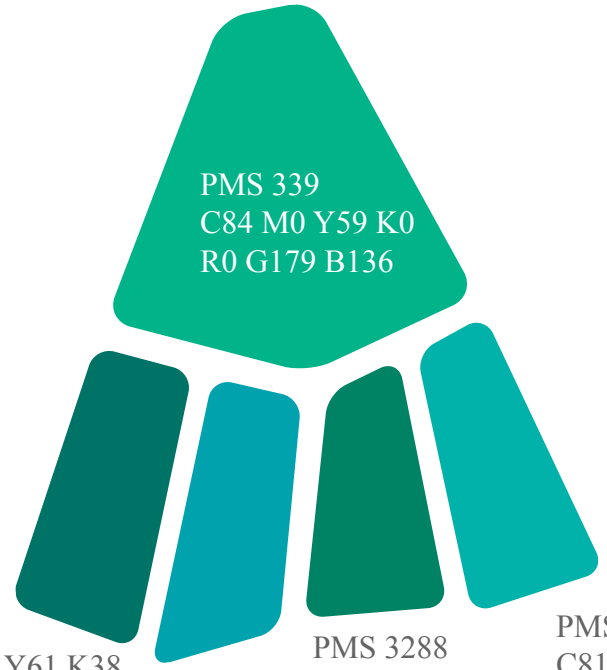
Platelet aggregation
-mass fractals with dimension 2 (slope ~ 2.1)
-open structure, branch-like aggregation
-age independent

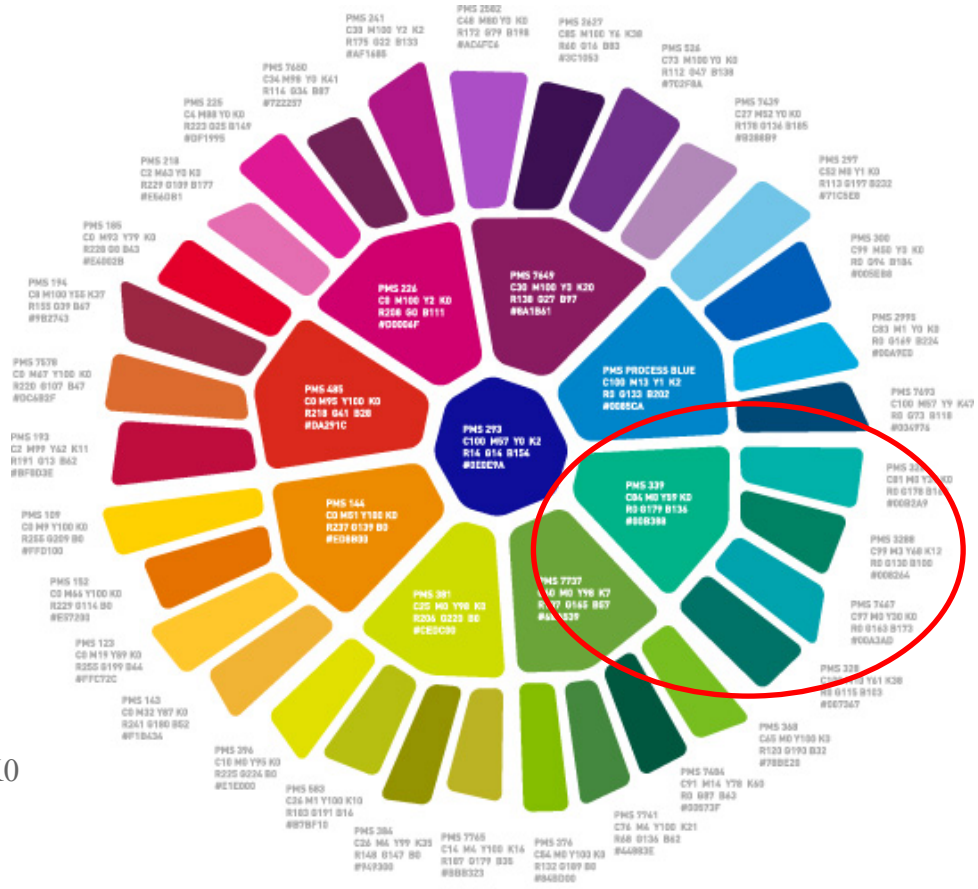
Surface morphology of the platelets
-rough surface (slope ~ 3)
-closed packed structure
-composition dependent

More insight needed by means of imaging methods to validate the aggregates morphology.

USING THE R&D COLOUR PALETTE

The chosen palette for R&D is the selected teal coloured segment below. Please click here to download the colour wheel.





COLOUR WHEEL (RGB)

Refer to the Unilever Visual Identity Standards Guide, pg. 25-31, for Introduction, Breakdown of Palettes (primary, secondary, tertiary), How to Use, Tints/Transparencies, Tone-on-Tone, and White Space.

USING ICONS

Use these icons for optional placement in your layout. You can scale them, crop them off a page, and change their colour. Please be sure to use the icons when they're relevant to a specific message.

*Refer to the **Visual Identity Standards Guide** on the Brand Centre for more details on proper use.*

USING ILLUSTRATIVE TYPE

To bring in more personality, use this optional lettering to highlight small amounts of text. Arrange each letter individuality to form words and phrases; scale them and change their colour. To help align text, turn on the grid lines in the menu bar under View.

*Refer to the **Visual Identity Standards Guide** on the Brand Centre for more details on proper use.*